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Microwave Dielectric Properties of $Ca_{1+x}Cu_3Ti_4O_{12+x}$ ($-0.04 \leq x \leq 0.04$) Ceramics

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Abstract

$Ca_{1+x}Cu_3Ti_4O_{12+x}$ ($-0.04 \leq x \leq 0.04$) ceramics were prepared by using conventional solid-state route. The microwave dielectric properties of the samples were investigated as a function of measured frequency and the Ca content. A pure perovskite structure was obtained for samples with $-0.02 \leq x \leq 0.02$, whereas small amount of CuO and $CaTiO_3$ appeared in the samples with x = -0.04 and 0.04, respectively, indicated that the solubility limit of Ca atom in CCTO lattice was reached for this system. Adjusting of Ca content showed a little influence on the microstructure of the ceramics. The sample with x = 0 exhibited good microwave dielectric permittivity (ε' ~ 85), which nearly constant at a broad frequency range of 1 – 35 GHz, then abruptly dropped to ~70 at 50 GHz. The other samples showed a strongly frequency dependence of dielectric permittivity from ~100 (at 1 GHz) to ~10 (at 50 GHz). The dielectric loss (tan-δ) for nonstoichiometry CCTO samples is relatively higher at least an order of magnitude and displays strong frequency dependence as compared with the x = 0 sample. The existence of vacancy (oxygen and Ca) and Ca/Cu disorder are the main factor affecting ε' and tan-δ values of the ceramics.

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Keywords: $CaCu_3Ti_4O_{12}$; nonstoichiometry; solid-state reaction; microwave dielectric properties

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1. Introduction

Recently, the advancement of microwave electronic applications, including wireless communications, satellite broadcasting systems and mobile telephones, makes rapid progress due to the enhanced performance of dielectric resonators e.g. filters, oscillators and antennas[1,2]. The requirements of dielectric ceramics used in dielectric resonators are high dielectric constant (ε_r), low dissipation factor (tan-δ) and near-zero coefficient temperature of resonance frequency (τ_f). These factors are correlated to the reducing size, frequency selectivity and temperature stability of the microwave electronic component. An example of the commercial dielectric ceramic is ferroelectric $BaTiO_3$-based, which shown strong Curie temperature dependent of ε_r, due to structural phase transition.

More recently, $CaCu_3Ti_4O_{12}$ (CCTO) ceramic has received most interest in dielectric resonators due to its colossal dielectric constant, CDCs ($\varepsilon_r \sim 10^4$), which nearly constant over a broad range of radio frequencies (RF; dc – 10 MHz) and temperatures (100 – 380 K), without associated with structural phase-transition[3,4]. It also exhibited low dielectric loss (tan-δ ~ 0.15 at 1 kHz) and good τ_f value (±15 ppm/°C)[5]. With decreasing temperature or increasing frequency, ε_r drops rapidly to a value of <100 and shows the Debye-type relaxation behaviour and the characteristic relaxation frequency follows approximately the Arrhenius law[4,6]. The ε_r value (approximately at 50 - 100) remains constant at a wide range of microwave frequency (MF; 1 – 35 GHz)[7], which becomes a good potential for reducing size of dielectric resonators. The size of compacted dielectric materials with high ε_r (>40) can be reduced significantly, without effected much by the high tan-δ value.

There are many techniques has been used to modify the dielectric properties of CCTO including ceramic processing [5,8], stoichiometry modification[7,9-17], dopants[18-20] and composites[2]. Among those techniques, stoichiometry modification seems to be an easier way to modify dielectric properties by creating crystal defects in CCTO such as vacancies and cation disorder substitutions. These defects could increase the resistivity of CCTO, which is one of important factor in increasing the permittivity. Studies on nonstoichiometry CCTO have been reported[7,9-17] and their dielectric properties at low frequency measurement have been improved. However, there is no study has been reported on the dielectric properties of CCTO with variation of Ca content at MF band.

Therefore, in order to improve the working frequency band, the microwave dielectric properties of CCTO with variation of Ca content is systematically investigated and explained.

2. Experimental details

CCTO samples were prepared by using the conventional solid-state reaction route from high-purity raw materials of CaO (>99% purity, Sigma-Aldrich), CuO (>99% purity, Sigma-Aldrich), and TiO_2 (>99% purity, Merck). The appropriate amounts of powders were prepared according to the nonstoichiometric ratio of $Ca_{1+x}Cu_3Ti_4O_{12+x}$ (where x = -0.04, -0.02, 0, 0.02, and 0.04), then dry-mixed in a rotary ball mill machine with ZrO_2 balls for 24 h. The mixed powders were calcined in air at 900 °C for 12 h, then pressed into a rectangular form (14 x 14 x 5 mm^3) before being sintered in air at 1040 °C for 10 h (heating and cooling rates of 5 °C/min). X-ray diffraction patterns of all samples were recorded using an X-ray diffractometer (XRD, Bruker AXS D8 Advance) with Ni-filtered Cu$K\alpha_1$ (λ = 1.54056 Å) radiation in a wide range of 2θ = 10 – 90°, a scanning speed of 2°/min, and a step width of 0.034. The identification and quantitative analyses of phase presence in XRD patterns were conducted by using the Rietveld refinement method using PANalytical X'Pert HighScore Plus software. The morphology characteristics of the samples were performed using a field-emission scanning electron microscopy (FESEM, SUPRA™ 35VP Carl Zeiss) equipped with energy dispersive X-ray (EDX) spectroscopy. Dielectric permittivity (ε') and tangent loss (tan-δ) were measured using microwave vector network analyser (PNA-X Network Analyser, 8720D) at room temperature.

3. Results and discussion

3.1. Phase structure and composition of the sintered CCTO samples

Fig. 1 shows room temperature XRD patterns of the $Ca_{1+x}Cu_3Ti_4O_{12+x}$ ceramics with different x, sintered at 1040 °C for 10 h, and their Rietveld refinement results are shown in Table 1. From both figure and table, CCTO

compound was identified in all samples as the main phase, which belongs to the body-centered cubic perovskite under *Im*3 space group and agreed-well with those reported in the ICSD file no. 005-8088. A single phase CCTO was detected in the $x = 0$ sample. By increasing or decreasing of x value to -0.02 and 0.02, respectively, the samples still retained a single phase and secondary phases started to appear at $x \leq -0.04$ (CuO; ICSD file no. 002-8611) and $x \geq 0.04$ ($CaTiO_3$; ICSD file no. 003-5181), indicates that the solubility limit of Ca atom in CCTO lattice was reached for this system. The result is consistent with the literature[14], with notion that no major defects mechanism related to CCTO solid solution. The lattice parameter (a) of the $x = 0$ sample is in good agreement with the ICSD file, comprised a value of 7.391 Å. However, it was reduced with decreasing of Ca content at $x = -0.02$, assign to the formation of Ca and/or oxygen vacancies, then shows a plateau trend when $x \leq -0.02$. The opposite result was observed in the CCTO with excess of Ca content, indicate that the disorder substitution of bigger Ca ions into Cu sites as proposed by many literatures[12-14]. The agreement indices value of R_{wp} and GOF are less than 6 and 4, respectively, indicates that the process is in good refinement analysis. It is worth to mention that these results is in good refinement process where the value of R_{wp} and GOF is under acceptable range of 20 and 4, respectively

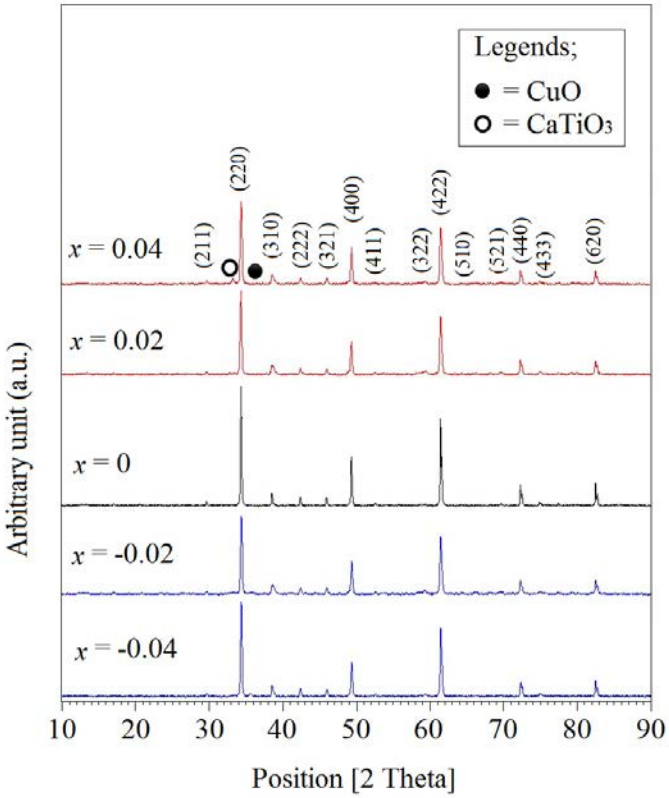

Fig. 1. XRD patterns of $Ca_{1+x}Cu_3Ti_4O_{12+x}$ ceramics with different Ca contents.

Table 1. Rietveld refinement results

x value	Phase composition (wt%)			Lattice parameter (a) of CCTO (Å)	Agreement indices	
	CCTO	CuO	$CaTiO_3$		R_{wp} (%)	GOF
-0.04	99.9	0.1		7.386	5.995	1.366
-0.02	100	-	-	7.386	5.633	1.158
0	100	-	-	7.391	5.733	1.173
0.02	100	-	-	7.394	5.963	1.382
0.04	99.8	-	0.2	7.394	5.819	1.206

3.2. Microstructure of the sintered CCTO samples

Fig. 2 depicts a series of FESEM image of surface $Ca_{1+x}Cu_3Ti_4O_{12+x}$ ceramics with different of *x*. Apparently, the morphologies changes significantly with the *x* value. As shown in Fig. 2.(a-b), ceramic with $x < 0$ show the microstructure of bimodal grain size distribution. When increasing the Ca content, there is a delicate decrease in the grain size, while retaining its bimodal grain size distribution. The present result is generally consistent with the reported microstructure for the Ca stoichiometry CCTO ceramic recently by Fang et al.[21].

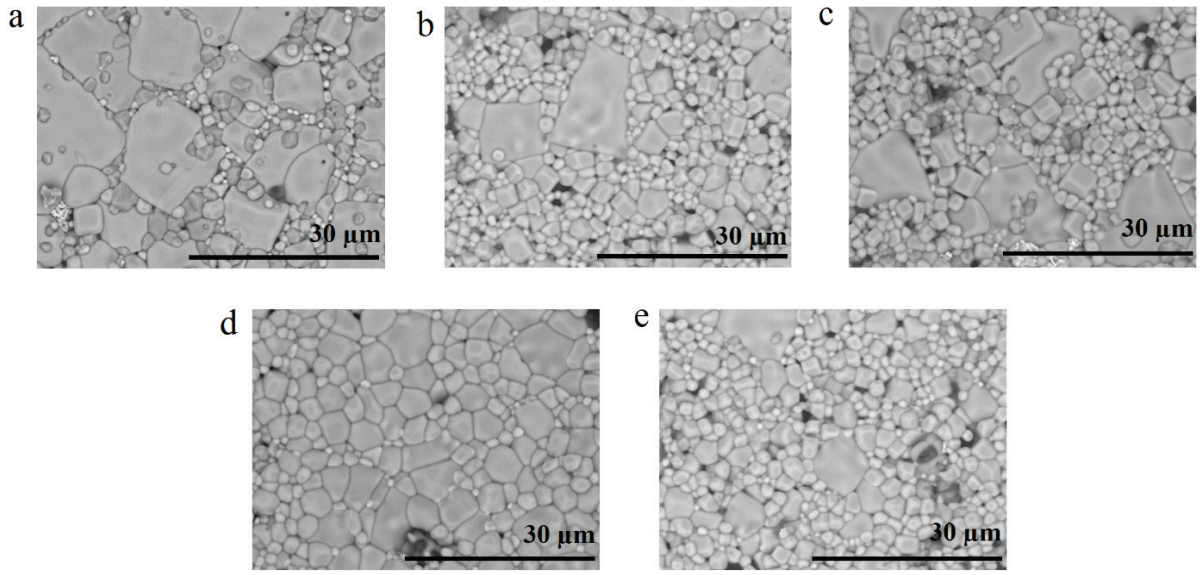

Fig. 2. FESEM image of $Ca_{1+x}Cu_3Ti_4O_{12+x}$ ceramics with different Ca contents (*x*); (a) -0.04, (b) -0.02, (c) 0, (d) 0.02 and (e) 0.04.

3.3. Microwave dielectric properties

Fig. 3 shows frequency dependence of dielectric permittivity (ε') and tangent loss (tan-δ) for CCTO samples with different in Ca contents. As can be seen from Fig. 3a, the ceramics display two behaviors of ε' value namely weak and strong of frequency dependent. The one with $x = 0$ exhibits a weak frequency dependent, where its ε' value is plateau about ~85 at a broad frequency range of 1 – 35 GHz, then rapidly dropped to ~70 at >35 GHz. However, the other samples with nonstoichiometry shows a strong frequency dependent, where their ε' values are rapidly dropped from ~100 at 1 GHz to ~10 at 50 GHz. The tan-δ value (Fig. 3.b) for nonstoichiometry CCTO samples is higher at least an order of magnitude as compared with the $x = 0$ sample.

It is noted that the impacts on the dielectric dispersion values at microwave frequencies contain intrinsic and extrinsic contributions. The intrinsic factors including lattice structure properties and lattice vibrational modes, while the extrinsic factors are generally related with defect concentration, impurities, porosity and grain size. The great different of microwave ε' value between nonstoichiometry and pure CCTO samples are not much affected by impurities, porosity and grain size. For impurities effect, it can be explained that ε' value for CuO (~18) and $CaTiO_3$ (~100) is nearly constant over a broad range of measured frequency[22], which is inconsistent with relative permittivity of multiphase ceramics[23] and also inconsistent with decreasing ε' value as a function of frequency. The porosity also did not much influence on the experimental permittivity, which can be eliminated according to $\varepsilon' = \varepsilon_{exp}(1 + 1.5.\text{porosity})$ formula[24]. The corrected permittivity usually slightly higher about ~1% than the experimental value. On the other hand, the effect of grain size is not much influenced, since the space charge polarization is no longer dominant at this MF region.

Based on the aforementioned above, the MF dielectric response can be originated from the lattice characteristics, defect concentration and the lattice vibrational modes (polarizability). For pure CCTO, the ε' value can be explained based on the hopping of electrons among copper ions of various valences or of O^{2-} ions around Cu^{1+}/Cu^{2+} or Ti^{4+} through vacant sites that will lead to the rotation of dipoles[20]. These vacant sites (oxygen and Cu) is a common phenomenon in titanate materials when sintered at high sintering temperature (>1000 °C)[25]. For nonstoichiometry CCTO, the great decreased of ε' value can be indicated to the different types of defect present, i.e. Ca and/or oxygen vacancy (*a* value is decreased) and disorder substitution of bigger Ca ions into Cu sites (*a* value is increased). The existence of these defects (vacancy and Ca/Cu disorder) with different Columbic charges reduced the hopping of charged carrier[13] and impede the rotation of dipoles.

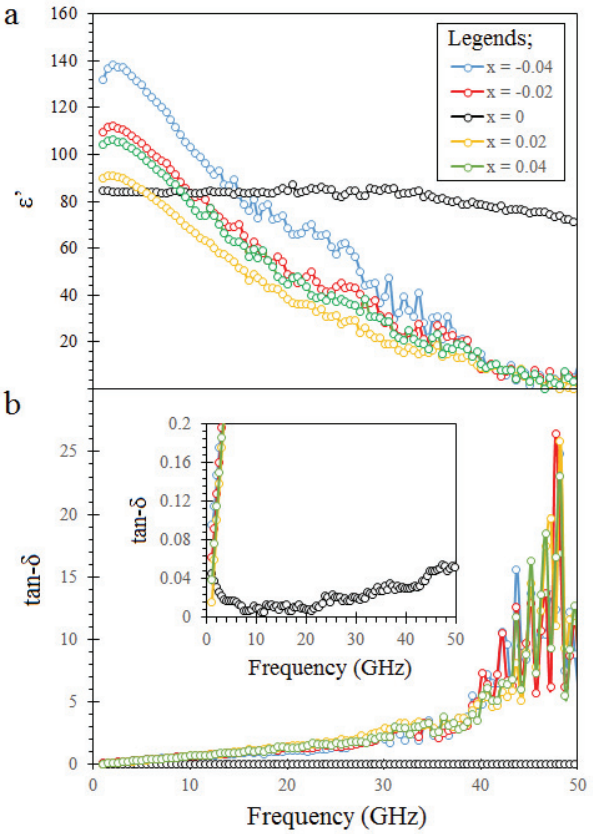

Fig. 3. Frequency dependence of (a) dielectric permittivity and (b) tangent loss for $Ca_{1+x}Cu_3Ti_4O_{12+x}$ ceramics with different Ca contents. The inset in the b is the expanded view of tan-δ

4. Conclusion

Microwave dielectric properties of $Ca_{1+x}Cu_3Ti_4O_{12+x}$ ($-0.04 \leq x \leq 0.04$) ceramics were investigated as a function of measured frequency and the Ca content. The pure perovskite structure was obtained for the samples with $-0.02 \leq x \leq 0.02$, whereas a small amount of CuO and $CaTiO_3$ appears in the samples with $x = -0.04$ and 0.04, respectively. Ca stoichiometry modification shows little influence on the phase structure and microstructure of the ceramics. The sample with $x = 0$ exhibits good microwave dielectric permittivity (ε' ~ 85), which nearly constant at a broad frequency range of 1 – 35 GHz, then abruptly dropped to ~70 at 50 GHz. The other sample shows a strongly frequency dependent of dielectric permittivity from ~100 (at 1 GHz) to ~10 (at 50 GHz). The tan-δ value for nonstoichiometry CCTO samples is relatively higher at least an order of magnitude and displays strong frequency

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